Supplementary information

Self-organized defect-rich RuMO_x epitaxial layers (M = Mn, Fe, Co, Ni, Cu) for catalytic applications

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1. Supplementary data



Fig. S1 XRD profiles of (a-b) 5Ru+0.5*M*/r-TiO₂ and (c-d) 5Ru/a-TiO₂.



Fig. S2 Ru K-edge (a) XANES and (b) FT-EXAFS for 5Ru+0.5*M*/r-TiO₂, 5Ru/r-TiO₂, and RuO₂.



Fig. S3 M K-edge WT-EXAFS for reference bulk materials.



Fig. S4 *M*2p XPS spectra of 5Ru+0.5*M*/r-TiO₂ and 0.5*M*/r-TiO₂: (a) M = Mn; (b) M = Fe; (c) M = Co; (d) M = Ni; (e) M = Cu.



Fig. S5 Ru 3d XPS spectra of 5Ru+0.5*M*/r-TiO₂: (0) raw data, (-) fitting data.



Fig. S6 H₂-TPR profiles of 5Ru+0.5Ni/a-TiO₂ and 5Ru/a-TiO₂.



Fig. S7 Ru K-edge (a) XANES and (b) FT-EXAFS spectra for 5Ru+0.5Ni/r-TiO₂ before and after the catalytic CO oxidation at 50°C. Ni K-edge (c) XANES, (d) FT-EXAFS, (e, f) WT-EXAFS for 5Ru+0.5Ni/r-TiO₂ before and after the catalytic CO oxidation at 50°C.



Fig. S8 TOF for CO oxidation reaction at 50°C over 5Ru/r-TiO₂, 5Ru+0.5Ni/r-TiO₂, 5Ru+0.5Ni/a-TiO₂, 5Ru+0.5Ni/ZrO₂, and 5Ru+0.5Ni/CeO₂.



Fig. S9 (a) Ni loading dependencies of the activity of 5Ru+xM/r-TiO₂ toward CO oxidation at 50°C. (b-c) HAADF-STEM images of (b) 5Ru+0.1Ni/r-TiO₂ and (c) 5Ru+5Ni/r-TiO₂. (d) LCF of XANES spectrum of 5Ru+5Ni/r-TiO₂. The best fit was achieved by linear combination of components 1 and 2. The respective contributions were 51% and 49%, respectively. (e) Power WT-EXAFS analyses of 5Ru+xNi/r-TiO₂ in a range of $R = 2.2 \sim 4.0$ and $k = 0 \sim 13.5$. WT-EXAFS for the respective catalysts are also given.

Sample in the literature	Misfit with r-TiO ₂ (%)		
	a = b	С	
Co-RuO ₂	1.9	3.3	
Ni-RuO ₂	1.5	4.2	
Cu-RuO ₂	1.8	4.4	
RuO ₂	2.2	4.9	

Table S1. lattice mismatches of M-RuO₂ (M = Co, Ni, Cu) and RuO₂ with r-TiO₂ shown in Fig. 2 in the manuscript.

^a Cited from the reference: L. Burnett et al., Chem. Mater., 32, 6150 (2020).

Sample	Peak label	Binding energy (eV)	Relative area (%)
	Mn ³⁺	641.6	57.2
5Ru+0.5Mn/r-TiO ₂	Mn^{4+}	643.1	42.8
	satellite		
	Mn^{3+}	641.1	56.4
0.5Mn/r-TiO ₂	Mn^{4+}	642.7	43.6
	satellite		
	Fe ²⁺	710.3	50.2
5Ru+0.5Fe/r-TiO ₂	Fe ³⁺	712.2	49.8
	satellite		
	Fe ²⁺	709.6	54.8
0.5Fe/r-TiO ₂	Fe ³⁺	711.8	45.2
	satellite		
	Co ²⁺	781.6	72.3
$5Ru+0.5Co/r-TiO_2$	Co ³⁺	780.5	27.7
	satellite		
	Co ²⁺	781.6	65.2
0.5 Co/r-TiO ₂	Co ³⁺	780.6	34.8
	satellite		
	Ni ²⁺	853.6	9.5
5Ru+0.5Ni/r-TiO ₂	Ni ³⁺	856.2	90.5
	satellite	861.8	
0.5Ni/r-TiO ₂	Ni ³⁺	855.8	100
	satellite	861.7	
5Ru+0.5Cu/r-TiO ₂	Cu ⁰ /Cu ⁺	932.7	51.9
	Cu^{2+}	933.8	48.1
0.5 Cu/r-TiO ₂	Cu^0/Cu^+	932.0	70.0
	Cu^{2+}	933.3	30.0

Table S2. Summary of curve fitting results for XPS spectra of $5Ru+0.5M/r-TiO_2$ and $0.5M/r-TiO_2$.

Ion	Electronegativity of ion
Ru ⁴⁺	19.80
Ti ⁴⁺	13.86
Mn^{3+}	10.85
Mn^{4+}	13.95
Fe ²⁺	9.15
Fe ³⁺	12.81
Co^{2^+}	9.40
Co^{3^+}	13.16
Ni ²⁺	9.55
Ni ³⁺	13.37
Cu^+	5.70
Cu^{2+}	9.50

 Table S3 Electronegativity of respective metal ions.

	O-1s XPS			
Sample	Dools Johol	Binding	$O_{latt} / O_{vac} / O_{ads}$	0 /0
	I Cak label	energy (eV)	(%)	Ovac/Olatt
	O _{latt}	530.2		
$5Ru/r-TiO_2$	O_{vac}	531.1	86.2/9.3/4.5	0.11
	O _{ads}	532.1		
	Olatt	530.3		
$5Ru+0.5Mn/r-TiO_2$	O_{vac}	531.2	69.7/25.1/5.3	0.36
	O _{ads}	532.3		
	O _{latt}	530.3		
5Ru+0.5Fe/r-TiO ₂	O_{vac}	531.2	75.2/21.0/3.8	0.28
	O _{ads}	532.3		
	Olatt	530.4		
$5Ru+0.5Co/r-TiO_2$	O_{vac}	531.3	63.7/31.3/4.9	0.49
	O _{ads}	532.9		
	Olatt	530.2		
5Ru+0.5Ni/r-TiO ₂	O_{vac}	531.0	77.9/18.7/3.4	0.24
	O _{ads}	532.3		
5Ru+0.5Cu/r-TiO ₂	O _{latt}	530.4		
	O_{vac}	531.3	71.8/22.8/5.4	0.32
	O _{ads}	532.5		

Table S4 Summary of O1s XPS spectra of 5Ru+0.5*M*/r-TiO₂. O₂ adsorption amount estimated from O₂-TPD for 5Ru/r-TiO₂ and 5Ru+0.5*M*/r-TiO₂.

Catalyst	Gas composition	GHSV (mL/g _{cat} /h)	Temp. (°C)	TOF (mol/mol _{metal} /h)	Ref.
5Ru/r-TiO ₂	0.5%CO-20%O ₂ -79.5%Ar	60000	50	4.8	this study
$5Ru+0.5Mn/r-TiO_2$	0.5%CO-20%O ₂ -79.5%Ar	300000	50	12.1	this study
5Ru+0.5Fe/r-TiO ₂	0.5%CO-20%O ₂ -79.5%Ar	300000	50	20.5	this study
$5Ru+0.5Co/r-TiO_2$	0.5%CO-20%O ₂ -79.5%Ar	600000	50	23.2	this study
5Ru+0.5Ni/r-TiO ₂	0.5%CO-20%O ₂ -79.5%Ar	600000	50	49.4	this study
$5Ru+0.5Cu/r-TiO_2$	0.5%CO-20%O ₂ -79.5%Ar	600000	50	25.7	this study
$5Ru/r-TiO_2$	1%CO-0.5%O ₂ -98.5%He	30000	55	<1	1
5Ru/CeO ₂ -NR-r	1%CO-20%O ₂ -79%He	36000	50	16.2	2
1Ru-CeO ₂ NF	1%CO-20%O ₂ -79%He	46000	50	24.7	3
m-5RuO ₂ 10CuO/CeO ₂	1%CO-21%O ₂ -78%N ₂	30000	50	3.0	4
Ru+CeO ₂	0.4%CO-10%O ₂ -89.6%He	600000	50	21.7	5
Ru/C12A7:e-	6.5%CO-4.7%O ₂ -88.8%He	25200	75	18.5	6
Ru/Graphene	0.05%CO-21%O2-78%N2	30000	50	0.15	7

 Table S5 Summary of catalytic activity toward low temperature CO oxidation.

Sample	BET surface area (m^2/g)
5Ru/r-TiO ₂	36.8
$5Ru+0.5Mn/r-TiO_2$	31.3
$5Ru+0.5Fe/r-TiO_2$	31.4
5Ru+0.5Co/r-TiO ₂	35.1
5Ru+0.5Ni/r-TiO ₂	34.2
$5Ru+0.5Cu/r-TiO_2$	34.9

Table S6. BET surface area for $5 Ru/r\mbox{-}TiO_2$ and $5 Ru\mbox{+}0.5 M/r\mbox{-}TiO_2.$

2. Additional discussions

2.1 Predictions of how the 3d-transition metal dope affects the lattice mismatch

For the hetero-epitaxy of crystal structures with a=b=c lattice parameters, e.g., fcc type crystal structures and so on, the lattice mismatch is simply defined as the following equation:

Lattice mismach (%) =
$$\frac{|a_{sub} - a_{EL}|}{a_{sub}} \times 100$$

, where a_{sub} and a_{EL} mean the lattice parameters of the substrate and epitaxial layer, respectively.

In the case for rutile type structure, it is not so simple because of $a = b \neq c$ lattice parameters. We can only describe the respective lattice mismatch in a = b and c. The lattice mismatches of *M*-RuO₂ (M = Co, Ni, Cu) and RuO₂ reported by Burnett et al. with r-TiO₂ are summarized as **Table S1**. We can see that 3d transition metal dope contributes to the reduction of the lattice mismatches with the rutile TiO₂ substrate by 0.3~0.7% in a = b and 0.5~1.6% in c.

2.2 Experimental verification of the importance of RuNiO_x-EL in the low-temperature CO oxidation

Among the supported Ru catalysts reported so far, $5Ru+0.5Ni/r-TiO_2$ has the highest TOF, demonstrating the high potential of heterometal dope-assisted epitaxial growth phenomena for engineering the surface reactivity of the epitaxy. The structure of the RuNiO_x epitaxial layer was stable under the reaction conditions, as shown in Ru and Ni K-edge XAFS data (**Fig. S7**). Furthermore, other supported catalysts, i.e., a-TiO₂, CeO₂, and ZrO₂ co-loaded with 5 wt% Ru and 0.5 wt% Ni, showed TOF less than 1/5 of 5Ru+0.5Ni/r-TiO₂ (**Fig. S8**). Therefore, the r-TiO₂ support is essential for the creation of the high activity toward low-temperature CO oxidation, supporting that the activity origin of 5Ru+0.5Ni/r-TiO₂ is related to the epitaxial growth phenomena.

As shown in the bulk M-RuO₂ composite oxides, the solid solution limits correspond to an M/Ru molar ratio of about $0.2^{.38}$ With this in mind, the *M* loading effect on the structure and catalytic activity was investigated to further and 5.0 were chosen as the candidate systems because of the noteworthy activity of 5Ru+0.5Ni/r-TiO₂. The relationship between the TOF of $5Ru+xNi/r-TiO_2$ and Ni co-loading is shown in Fig. S9a as red dots. Even with 0.1 wt% Ni doping (Ni/Ru molar ratio = 0.03), the TOF increased from 4.8 mol/mol_{metal}/h to 28.9 mol/mol_{metal}/h. The Ni loading that gave the maximum TOF was 0.5 wt% responsible for Ni/Ru molar ratio = 0.17, consistent with the Ni solid solution limit reported in the literature.³⁸ The TOF decreased with a further increase in the Ni loading, reaching 7.5 mol/mol_{metal}/h at the Ni loading of 5.0 wt% (Ni/Ru molar ratio = 1.7). A similar trend was also observed for the reaction rate (the conversion rate of CO (mol/h) normalized by the catalyst loading (gcat): Fig. S9a, blue dots), indicating that the highly active reaction field is related to the metal oxides specifically formed at Ni co-loading responsible for the Ni solid solution limit. HAADF-STEM images of $5Ru+xNi/r-TiO_2$ (x = 0.1, 0.5, and 5.0) revealed that RuNiO_x-EL was dominant in 5Ru+0.1Ni/r-TiO₂ and 5Ru+0.5Ni/r-TiO₂, while RuNiO_x-EL was negligible, instead, NiO particles were dominant in 5Ru+5Ni/r-TiO₂ (Figs. S9b and c). Linear curve fitting for the XANES spectrum of 5Ru+5Ni/r-TiO₂ revealed fractions of NiO and Ni-doped into the RuO_x epitaxy as 51% and 49%, respectively (Fig. S9d). In WT-EXAFS of 5Ru+5Ni/r-TiO₂ (Fig. S9e), the Ni-(O)-Ni backscattering specific to bulk NiO was observed at $(k, R) = (5.6 \text{ Å}^{-1}, 2.5 \text{ Å})$ with a high WT-coefficient. Power WT in an R range of Ni-O-Ni and Ni-O-Ru, i.e., 2.2-4.0 Å provided quantitative information on the contributions of their backscattering and demonstrated the significant contribution of Ni-O-Ni backscattering as compared with the cases for 5Ru+0.1Ni/r-TiO₂ and 5Ru+0.5Ni/r-TiO₂ (**Fig. S9e**). It can be rationalized by considering that the excess co-loading of Ni (> Ni solid solution limit: 0.17 wt%) leads to the decomposition of the epitaxy and aggregations of NiO with low efficiency of the formation of RuNiO_x composite oxides. By contrast, XAFS data of 5Ru+0.1Ni/r-TiO₂ were closely similar to those of 5Ru+0.5Ni/r-TiO₂ because the RuNiO_x-ELs were dominantly formed in both catalysts due to the Ni co-loading in a range of the Ni solid solution limit. Accordingly, the RuNiO_x-ELs are specifically formed in the region of the Ni solid solution limit, and thereby activity improvement was observed in the region, supporting the importance of RuMO_x-EL in the catalytic oxidation of CO at low temperature.

3. Supplementary references

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